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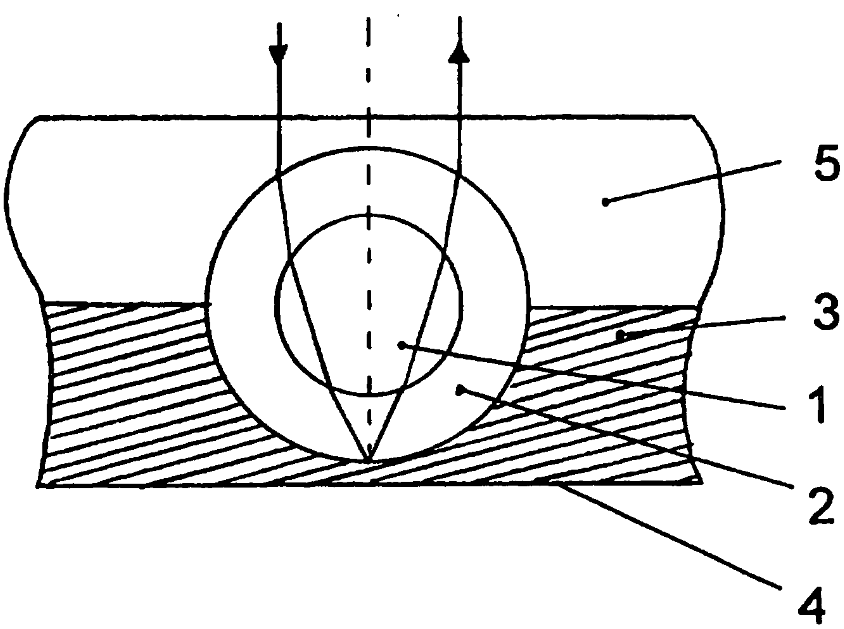
(54) Title: SPHERICAL BEADS FOR LIGHT RETRO-REFLECTIVE APPLICATIONS AND METHOD OF PREPARING SUCH BEADS




(57) Abstract

The invention relates to a method of preparing spherical beads for light retro-reflective applications, where the beads are coated with a transparent distance layer and possibly a light reflective coating. The invention also relates to a spherical bead (1) for use in light retro-reflective applications, where said bead is coated with a transparent distance layer (2) and possibly a light retro-reflective material (6).

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Spherical beads for lighb retro-reflective applications and method of preparing such beads

The present invention relates to spherical beads for light retro-reflective applications and a method for preparing such beads. More specifically, the invention relates to a controlled coating of optical glass beads for the use in combination with different types of substrate materials, such as foils, metals, textiles, paper, etc.

Within the technical field of retro-reflection, there is common practice to use glass beads of different refractive indexes as light refractive elements. In many applications, it is essential that the light refractive element is placed at an exact distance with respect to a reflecting surface. The distance between the outer surface of the glass bead and the light reflecting layer is commonly defined as the space layer or the distance layer. Having space layers of well defined thickness is of great importance, as the bead may be enveloped by different polymer materials that will limit the relation between the refractive indexes in the glass bead and the polymer material. For instance, if the embedding medium is air having a refractive index of 1,0, the use of a space layer should normally not be necessary. Polymers have a refractive index of approx. 1,3 to approx. 1,7 necessitating a space layer when combined with the most common types of glass, if an acceptable focus of the light rays on the reflector should be obtained.

One traditional way of obtaining a space layer on the back side of a mono-layer of glass beads, is to apply a layer of polymer materials such as transparent lacquers, polymeric melts etc. Meanwhile, the resulting space layer provided according to said method may often vary both with respect to the thickness and how the layer actually embeds the beads. If the layer embeds the beads in an insufficient manner, then the retro-reflective properties will be very poor especially at sharp angles of incidence.

The invention as claimed is intended to remedy these drawbacks. It solves the problem of how to obtain an accurate space layer between the bead and the reflecting material. Further, according to the invention good reflective properties may be obtained at very

sharp angles, close to 180 degrees. Still further, according to the invention cheap glass beads with low refractive angles may now be used in retro-reflective applications where good reflective properties are required.

In the following, the invention will be further described by means of examples and with reference to the drawings in which:

Figure 1 shows a spherical bead according to the invention in a retro-reflective application, and

Figure 2 shows a spherical bead according to the invention, partly coated with a reflective layer.

It is a well known problem to achieve a homogeneous defined and consistent coating onto a small spherical particle. This is particularly so when dimensions of the particle are of the same magnitude as the coating layer, e.g. a homogeneous evenly distributed coating of 30 μm thickness onto a particle with mean radius of 35 μm is relatively difficult to obtain.

To achieve a polymeric coating in an economic way it may be used spray drying techniques, fluidized bed techniques, or preferably a combination of the two said techniques. Spray drying is effective but unfortunately it suffers from poor layer thickness consistency and agglomeration. This leads to a process difficult to control. Fluidized bed technology is also effective, but suffers from basically the same drawbacks as spray drying.

Preferably a coating technique of combined fluidized bed and spray drying is used. This combination does not suffer from the above mentioned drawbacks, and is very valuable as the thickness of the layer in some cases should be up to three times the diameter of the bead. Typically, the layer thickness is in the range as follows;
$d/10 < t < 3d$, where $t$ = layer thickness, $d$ = diameter of the bead.

According to one preferred method of coating, the glass beads are circulated in a vessel in a gas stream using fans. The fan blows the glass beads upwards through an opening

where in addition a nozzle is placed. From the nozzle a polymeric solution or dispersion is atomised to tiny droplets. The droplets are carried by the gas stream together with the glass beads. The droplets have approximately the same speed as the glass beads, and they are substantially smaller. As these particles are carried upwards the atomised droplets precipitates onto the glass beads. When all droplets have precipitated onto the glass beads, these fall down to the bottom of the vessel where the process starts again and is then repeated until the preferred coating layer is achieved. The coating will therefore consist of numerous small droplets altogether forming a continuous layer or film spherically surrounding the glass bead, where said layer may dry and harden in the run of the process.

In a similar manner, a light reflective layer can be applied to the beads. Such layers may typically consist of a polymeric coating with metallic pigments, and may comprise resin, aluminium flakes, crosslinker, catalyst, solvent and flow additive.

Preferably, the coated beads with the surrounding layer or film are treated for instance thermally in the succeeding application process, the film thus forming a homogenous and perfect spherical shape. This contributes to give the coated beads very promising optical properties.

Figure 1 shows a spherical bead 1 coated with a transparent layer 2. The coated bead may form part of a mono layer of plural beads (not shown) that is partly embedded in a reflective layer 3 carried by a substrate 4. On top of the mono layer of spherical beads a transparent layer 5 can be applied. Such transparent layer can be applied by using rollers or preferably by means of coil coating and if so the transparent layer is made by a polymer coating. Alternatively, the layer may be applied by means of foil, or possibly by a powder coating system. Polymer coatings typically comprises resin, solvents, crosslinker, catalyst and flow additive. Said transparent layer is smooth and is intended to provide satisfactory surface properties to the finished product. It might be coloured and may consist of several layers. Also a polymeric foil laminated to the layer of spherical beads can be employed as a top layer.

Figure 2 shows a spherical bead 1 coated with a transparent layer 2 together with a reflective layer 6 that partly covers the bead. In this example, the bead is embedded in

a layer 7 on a substrate 4. As in the foregoing example, the bead shown can form a part of a mono layer, that is coated with a transparent layer 5. When arranging this type of coated spherical beads in a mono layer, the light reflecting material on the upper surface of the beads in the mono layer must be removed. The light reflecting material is thus partly removed by mechanical, chemical or thermal means. This results in a mono layer of spherical beads having a light reflecting material at the parts turning towards the substrate and not at the parts now making the upper surface of the beads. Thus, there is provided discrete elements with built-in reflective properties that will not be influenced by the material embedding the lower surface of the sphere. This is very advantageous, as the embedding material 7 may be coloured by pigments, for instance to increase the lightness/brightness of the object produced.

According to the invention, each spherical bead is coated by a transparent coating and/or subsequently by a light reflecting material like for instance a metallic coating. Thus, coated spherical beads will have a shell acting as a space layer to provide relevant optical properties for each spherical bead.

Further, the application of the coated beads in a dispersion or a lacquer typically comprising resin, solvent, crosslinker, catalyst, and anti-settling agent, will sustain better stability against settling, as the coated beads will have a lower density compared to non-coated beads.

Transparent lacquers and metallics used in this invention as space layer and reflective coatings can be composed of different film forming polymers and/or dispersions.

Applicable polymer solutions are polyesters, polyurethane's, acrylics, epoxies, phenolics, polycarbonates, fluorocarbons etc. where the polymeric backbone can be functional to give thermosetting or thermoplastic properties.

Polymer dispersions and the like, having properties close to the solution product may be used and are usually but not necessary water based or water carried. These can be composed by the same polymeric compounds described above.

## Claims

1. A method of preparing spherical beads, such as glass beads, for light retro-reflective applications
characterized in that each spherical bead is coated with a transparent layer, that acts as a distance layer between the surface of the bead and the surface of a light reflective material.

2. A method according to claim 1,
characterized in that the distance layer is built up to have a thickness (t) within the range $d/10 < t < 3d$, where (d) is the diameter of the bead.

3. A method according to claim 1-2,
characterized in that the bead is coated with a light reflective material.

4. A method according to claim 3,
characterized in that the light reflective material on the surface of the spherical beads is partly removed by mechanical, chemical or thermal means.

5. A method according to claim 1-4,
characterized in that the spherical beads are coated by being subjected to an air or gas stream containing droplets of the coating that are sprayed into the gas stream by a nozzle, whereby the droplets adhere successively to the beads.

6. A spherical bead, such as a glass bead, for use in light retro-reflective applications,
characterized in that the bead (1) is coated with a transparent layer, such as a polymer, that acts as a distance layer (2) between the surface of the bead and the surface of a light reflective material (6).

7. A spherical bead according to claim 6, characterized in that the thickness (t) of the distance layer (2) is within the range $d/10 < t < 3d$, where (d) is the diameter of the bead (1).

8. A spherical bead according to claim 6-7, characterized in that the bead (1) is coated with a light reflective material (6), such as a polymeric coating with metallic pigments.

9. A spherical bead according to claim 8, characterized in that the the bead (1) is partly coated with the light reflective material (6).

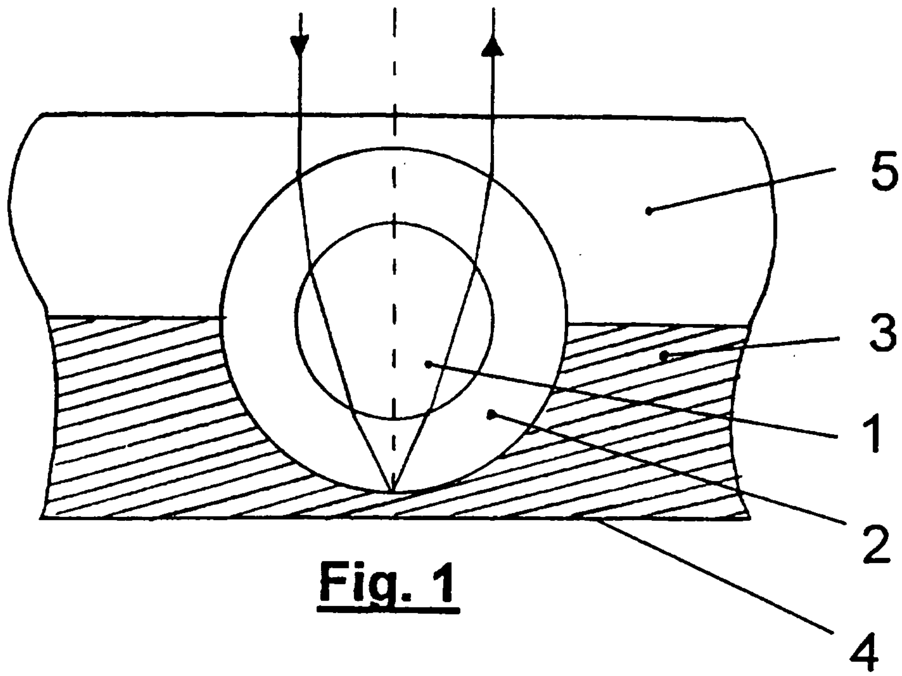


Fig. 1

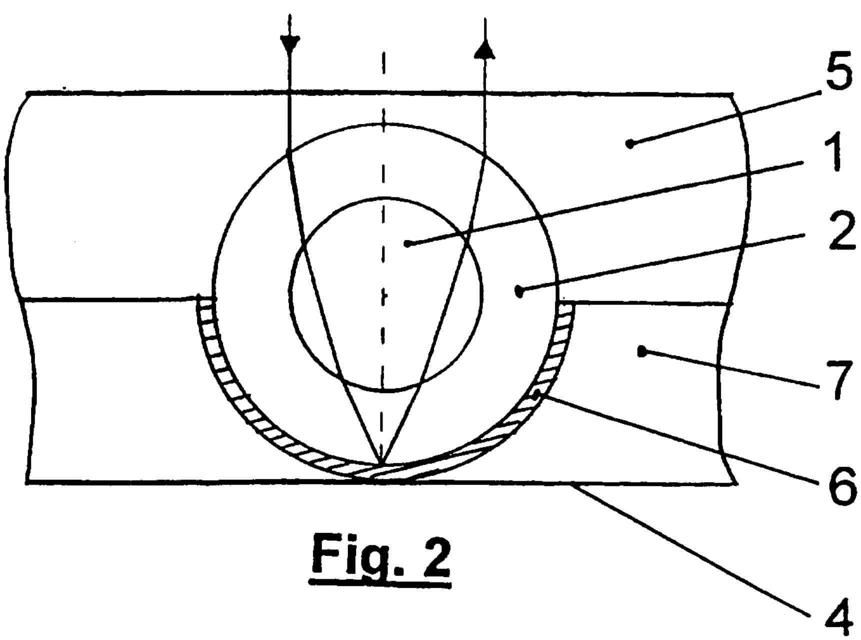


Fig. 2

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00300

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC6: C03C 12/02, G02B 5/128
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B44F, C03C, G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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☐ Further documents are listed in the continuation of Box C.  ☒ See patent family annex.

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| 14 March 1997 | 05 April 1997 (05.04.97) |

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# INTERNATIONAL SEARCH REPORT
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| Patent document cited in search report | | Publication date | Patent family member(s) | | Publication date |
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